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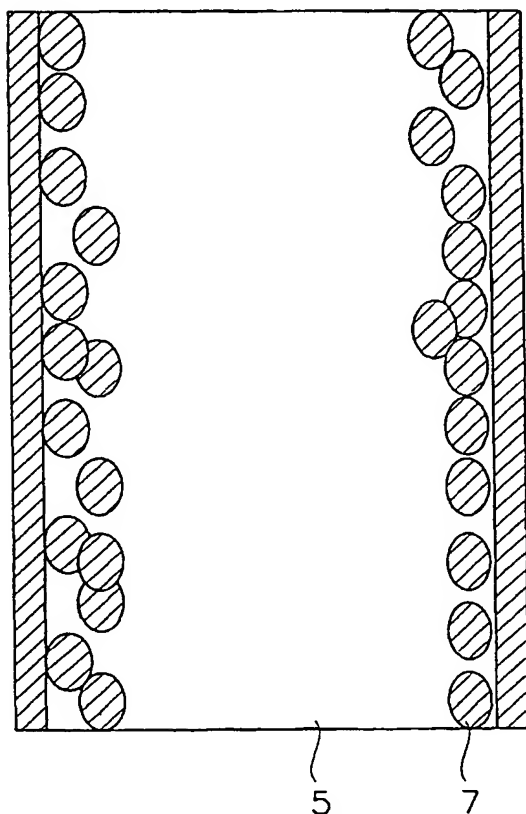
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(54) Title: ELECTROCHEMICAL CELL AND METHOD OF MANUFACTURING THEREOF



(57) Abstract: Disclosed are an electrochemical cell having excellent characteristics of impregnation with electrolytic solution and a method for manufacturing the same. The cell includes an anode, a cathode and polymer separation membrane installed between an anode and a cathode through polymer binder membrane. The polymer separation membrane is manufactured by forming polymer membrane including polyvinylidene-based polymer onto the supporting body of separation membrane. After extracting process of plasticizer, compressing process is implemented, so that plasticizer can be eliminated completely. Also, the polymer membrane is thin, so that non-uniformity of the manufacturing process is minimized. The polymer binder having a good adhesiveness is used, so that the attachment between electrode and separation membrane is practicable even at a low temperature. Additionally, since binding is a spot binding, a cell having good characteristics of impregnation with an electrolytic solution and a good performance is provided.

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ELECTROCHEMICAL CELL AND METHOD OF MANUFACTURING THEREOF

Technical Field

5 The present invention relates to an electrochemical cell and a method of manufacturing the same, and more specifically, to an electrochemical cell including a separation membrane having porous polymer membrane and a separation membrane supporter, and a method of manufacturing the same.

Background Art

10 A Lithium ion battery is used frequently for portable equipments such as cellular phone. A lithium polymer secondary battery becomes a substitute of conventional lithium secondary battery having defects such as a leakage of electrolyte, explosion, etc. and has advantage of variability in design. Also, instead
15 of metal can packing materials, aluminum pouch can be used. Accordingly, as compared with a case of using metal can package material, weight and energy density per unit volume can be improved, so that such merits a light and thin battery may be manufactured due to such merits.

20 As a proposal for lithium polymer secondary battery, a method has been suggested by Bell Communication Research, Inc. wherein porous polymer membrane is manufactured by extracting plasticizer included in the polymer. Also, a method wherein polymer membrane keeps electrolytic solution without extracting plasticizer was suggested.

25 U.S. Pat. No. 6,235,006 discloses a cell manufactured by dispersing a PVdF polymer onto an electrode without a plasticizer, forming a gap by using a nonsolvent, and compressing the resultant at a room temperature. However, in accordance with the disclosure in the above patent, it is difficult to impregnate the cell with an

electrolytic solution, because the compression of an electrode and a polymer membrane with heat may result in a separation of electrode from the polymer membrane as the lapse of time. Additionally, there may be a stability problem due to a minor-short-circuit resulted from non-use of inorganic additives. Also, the polymer
5 membrane is prepared by immersing the electrode into a non-solvent so that the electrode may be influenced by impurities, and a continuous manufacturing process is not practicable for a mass production.

U.S. Pat. No. 6,218,051 discloses a technology wherein a PVdF polymer membrane including a plasticizer and a porous separation membrane are thermally
10 compressed together with an anode and a cathode. In the said patent, since dibuthylphthalate (DBP) used as plasticizer is extracted after the compression with heat, it is difficult to completely remove the plasticizer. Thus, good productivity cannot be obtained due to a low mass production.

U.S. Pat. Nos. 5,720,780, 5,460,904, 5,456,000, and 5,418,091 disclose
15 technologies that a cell is manufactured wherein a polymer membrane prepared by adding silica particle and dibuthylphthalate as a plasticizer onto PVdF is thermally compressed onto an electrode. Pores for impregnation with electrolytic solution is subsequently formed through dipping the cell into a solvent enabling to dissolve DBP and then extracting DBP from the cell. In this case, due to the compression of
20 the polymer membrane with the electrode, impregnation with the electrolytic solution and complete removal of the solvent and plasticizer used for extracting process are difficult. Also, because of shrinkage of the polymer membrane, it is unreliable. Further, due to a low mass production rate and difficulties in regulation of production factor, it cannot be easily applied to a practical industry.

25 The critical problem in the above technology is that in order to suppress the shrinkage of polymer in the process of extraction of the plasticizer, a process for compression of the polymer membrane onto the electrode with heat is implemented.

This results in incomplete removal of the plasticizer during a process of extraction of the plasticizer. Additionally, during the impregnating process with the electrolytic solution as a post process, a long period of time is required, in turn, uniform impregnation is difficult, so that uniform interface between the electrode and the polymer membrane may be hardly obtained.

In case where a polyolefin-based porous separation membrane and polymer used for lithium secondary battery are combined, the temperature for the thermal compression is varied depending on the contents of the inorganic additives, but generally at a temperature higher than 120°C the thermal compression is performed. Accordingly, when a polyolefin-based porous separation membrane is used, physical properties of the supporting member can be changed. Also, since during the mass production a long time is required for extracting plasticizer, the reliability of extraction is insufficient, mass productivity is low and controlling factors for the mass production is difficult. In a case of not using the porous separation membrane, due to uneven thickness, a problem of short-circuits occurs seriously.

U.S. Pat. Nos. 5,853,916, 5,716,421, 5,834,135, 5,681,357 and 5,688,293 disclose a method for manufacturing a polymer battery wherein the extracting process of the plasticizer is not necessary. According to the disclosures in the above patent, after a polymer material is dispersed onto porous separation membrane having a good mechanical strength, the resultant is thermally compressed onto the electrode. Then, the cell is dipped into an electrolytic solution so that the cell may be impregnated with the electrolytic solution. Since a long period of time is required for the impregnation with the electrolytic solution due to the thermal compression of the electrode, the productivity is lowered.

Disclosure of the Invention

To solve the above problems of the prior art, it is an object of the present

invention to provide an electrochemical cell having a porous separation membrane wherein the porous membrane has a good mechanical strength, a good adhesiveness with the electrode, good absorption, and good electrolyte maintenance characteristics so that the electrochemical cell has a high capacity, a good cycle-life
5 characteristic.

Another object of the present invention is to provide various and easy methods for manufacturing the above electrochemical cell.

To accomplish the object, there is provided in the present invention an electrochemical cell comprising an anode; a cathode; and a separation membrane
10 which is installed between the anode and the cathode. The separation membrane includes a supporting body of the separation membrane. A polymer membrane is formed on the supporting body, and a polymer binder membrane is formed on the polymer membrane. The supporting body includes a polyvinylidene fluoride-based polymer.

15 The other object of the present invention is accomplished by a method comprising following the steps of forming a polymer membrane including a polyvinylidene fluoride-based polymer on a supporting body of a separation membrane; forming a polymer binder membrane by coating a polymer binder on the polymer membrane; and thermally compressing an anode and a cathode on the
20 polymer binder membrane at a temperature in the range of about room temperature to 80 °C.

Brief Description of the Drawings

The above objects and advantages of the present invention will become more
25 apparent by describing preferred embodiments in detail with reference to the attached drawings in which:

FIG. 1 is a cross-sectional view of a separation membrane manufactured

according to a preferred embodiment of the present invention;

FIG. 2 is a cross-sectional view of a separation membrane manufactured according to another preferred embodiment of the present invention;

FIG. 3 is a schematic cross-sectional view of a packing type lithium secondary
5 battery including a polymer separation membrane according to the present invention;

FIG. 4 is a schematic cross-sectional view of a stack type lithium secondary battery in the form of a stacked mono cell including a separation membrane according to the present invention;

10 FIG. 5 is a graph illustrating a relationship between a thickness-reducing rate of a polymer membrane and a final polymer membrane after extracting plasticizer during manufacturing the cell according to Example 1, and polymer contents according to thickness changes;

FIG. 6 is a graph illustrating a discharge capacity resulted from charging and
15 discharging of a cell in a rate of 1C depending on extracting time of plasticizer when a cell is manufactured according to Example 1;

FIG. 7 is a graph illustrating a voltage profile dependent on time during charging and discharging the lithium polymer battery by 0.2 C rate according to Example 1;

20 FIG. 8 is a graph illustrating a charging and discharging efficiency dependent on cycle during charging and discharging the lithium polymer battery by 1.0 C rate according to Example 1;

FIG. 9 is a graph illustrating a discharging capacity dependent on cycle during charging and discharging the lithium polymer battery by 1.0 C rate according to
25 Example 1;

FIG. 10 is a graph illustrating a discharging capacity dependent on cycle during charging and discharging the lithium polymer battery by 1.0 C rate according to

Example 4; and

FIG. 11 is a graph illustrating a discharging capacity dependent on cycle during charging and discharging the lithium polymer battery by 1.0 C rate according to Example 5.

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Best Mode For Carrying Out the Invention

The present invention provides an electrochemical cell comprising an anode; a cathode; and a separation membrane which is installed between the anode and the cathode, the separation membrane including a supporting body of the separation
10 membrane, a polymer membrane formed on the supporting body, and a polymer binder membrane formed on the polymer membrane, the supporting body including a polyvinylidene fluoride-based polymer.

Particularly, a thickness of the polymer membrane is preferably about 1 to 50 μm and the polymer binder membrane is preferably coated on a surface of the
15 polymer membrane such that the polymer binder membrane covers about 1-80 % of the surface of the polymer membrane.

The present invention provides a method comprising the steps of forming a polymer membrane including a polyvinylidene fluoride-based polymer on a supporting body of a separation membrane; forming a polymer binder membrane by
20 coating a polymer binder on the polymer membrane; and thermally compressing an anode and a cathode on the polymer binder membrane at a temperature in the range of about room temperature to 80 °C.

The polymer membrane may be manufactured by various methods as follows.

Firstly, the polymer membrane may be prepared by preparing a polymer
25 solution by mixing about 100 parts by weight of the polyvinylidene fluoride-based polymer, about 100-3,000 parts by weight of a solvent, and about 100-1,000 parts by weight of a plasticizer, coating the polymer solution on a supporting body of the

separation membrane, volatilizing the solvent from the coated polymer solution, and extracting the plasticizer using an extraction solution.

Secondly, the polymer membrane may be prepared by preparing a polymer solution by mixing about 100 parts by weight of the polyvinylidene fluoride-based polymer with about 100-3,000 parts by weight of a solvent, coating the polymer solution on a supporting body of the separation membrane, volatilizing the solvent from the coated polymer solution, and forming a pore by using a nonsolvent.

Thirdly, the polymer membrane may be prepared by preparing a polymer solution by mixing about 100 parts by weight of a polyvinylidene fluoride-based polymer, about 100-3,000 parts by weight of a solvent, and about 100-1,000 parts by weight of a plasticizer, coating the polymer solution on a separate membrane to form a layer by using a doctor blade method, attaching the coated layer to a supporting body by thermally compressing the coated layer and the supporting body at a temperature in a range of about room temperature to 130 °C, and extracting the plasticizer using an extracting solution.

Fourthly, the polymer membrane may be prepared by preparing a polymer solution by mixing about 100 parts by weight of a polyvinylidene fluoride polymer with about 100-3,000 parts by weight of a solvent, coating the polymer solution on a separate membrane to form a layer by using a doctor blade method, attaching the coated layer to a supporting body of the separation membrane by thermally compressing the coated layer and the supporting body at a temperature in a range of about room temperature to 130 °C, and forming a pore by using a nonsolvent.

The present invention will be described in detail with reference to the attached drawings below.

The separation membrane coated with a polymer is prepared as follows.

As the polymer materials employed in the polymer membrane, PVdF homopolymer or copolymer can be used. Since the homopolymer has a poor ionic

conductivity due to a high crystallization degree, a copolymer having hexafluoro propane (HFP) unit, preferably, HFP unit of 8-25% is used. The polyvinylfluoride-based polymer has good mechanical properties and a high ionic conductivity at a room temperature, and therefore the polyvinylfluoride-based polymer is highly recommended.

The polymer solution is prepared by dissolving the polymer into an appropriate solvent. As for a preferable solvent, acetone, tetrahydropurane, methylethylketone, dimethylformamide, dimethylacetamide, tetramethylurea, dimethylsulfoxide, triethylphosphate, trimethylphosphate, normalmethylpyrrolidone, etc. can mentioned. A mixed ratio of the polymer with respect to the solvent is about 1 : 1~30 by weight.

As for a plasticizer, dibuthyl phthalate (DBP), dimethyladipate, etc. can be used. In the present invention, whether or not to add plasticizer depends on manufacturing method of separator membrane. When it is added, mixed ratio of the polymer with respect to the plasticizer is about 1 : 1~10 by weight.

An inorganic filler such as SiO_2 , zeolite, Al_2O_3 and the like may be added into the solution. When the inorganic filler is added thereto, the mixed ratio of the polymer with respect to the inorganic filler is about 1 : 0.5~2 by weight and a size of the inorganic filler is favorably no more than 10 μm .

The obtained polymer solution is mixed in a solvent, preferably acetone, for approximately 3-24 hours through ball mixing or physical stirring and the like. This mixing can be performed at a room temperature, but the temperature can be somewhat raised to a temperature of about 40 to 60 °C for uniformly mixing the polymer solution. The inorganic additive and the plasticizer can be added thereto during stirring.

The stirred polymer solution is coated onto a supporting body of separator membrane.

As a supporting body of the separator membrane that can be used in the present invention, conventionally used non-woven polyethylene, non-woven polypropylene, woven PTFE, polyester non-woven fabric, solvent-spun-rayon, regenerated cellulose fiber, glass fiber, manila hemp, sisal pulp and kraft pulp, etc. may be mentioned.

5 These can be used alone or in a combination thereof.

Preferably, the woven separation membrane that has a high ionic conductivity and a good absorption capacity and may be impregnated with an electrolytic solution can be used. The porous membrane that is generally used has a small number of gaps and a poor electrolyte absorption capacity. However, when the woven separation membrane is used, the electrolyte absorption capacity is enhanced and the ratio of the area where ion is transferred at the interface with the polymer is high, so that good capacity and cycle-life characteristic can be obtained. Additionally, since the woven separation membrane is less expensive than a conventional separation membrane, manufacturing cost can be reduced. Also, a surface of the woven separation membrane is coarse, the shrinkage of the polymer membrane is prevented when it is used for a supporting body. Among the above-mentioned supporting bodies, even though the non-woven polyethylene and the non-woven polypropylene do not belong to the woven separation membrane, these can show good functions, and thus may be used in the present invention.

20 For reference, in case of the conventional Bellcore process, if an adhesiveness between the polymer and the electrode is decreased after the polymer is thermally compressed to the electrode, the shrinkage of the polymer occurs. Therefore, the cell is not reliable.

25 There are two methods for coating the polymer solution onto the separation membrane. As a first method, the solution is directly coated onto the supporting body of the separation membrane through a spray method, a doctor blade method, a screen-printing method and the like. The coated separation membrane is transformed

into the separation membrane including polymer membrane through volatilization of a solvent. In the thus prepared separation membrane, a pore is formed by using a nonsolvent when the separation membrane does not include a plasticizer and a pore is formed by using an extracting solvent when the separation membrane includes a plasticizer.

As a second method, using the above polymer solution, a layer is formed via a doctor blade method, on the supporting body of the separation membrane, preferably, a polyester film (for example, Mylar film that is commercial trade name), on which silicon has been coated. At this time, the polymer is coated to a thickness of about 1-50 μ m and more preferably to a thickness of no more than 10 μ m. The process for thermal compressing the polymer membrane on the supporting body of the separation membrane is implemented at about room temperature to 130°C and the required period of time depends on the pressure and the temperature for the thermal compression. For example, when they are compressed by using a roll at a temperature of about 100°C, a speed of at least 10m/min is practicable. Preferably, a compressing ratio is about 1-75% of a total thickness.

In any method of the above methods, if the plasticizer is added for increasing the porosity, the plasticizer is extracted after the polymer has been coated on the supporting body. In order to increase the porosity, when a plasticizer is not added, characteristics of a nonsolvent is utilized. In both methods, as for the solvent, hexane, pentane, toluene, methanol, ethanol, carbon tetrachloride, o-dichlorobenzene, trichloroethylene, water and the like can be used. At this time, in the both cases, staying time in the solvent preferably does not exceed 5min. This can resolve some problems of mass production, which are issued in the conventional Bellcore process.

According to the present invention, since a thickness of a polymer coated on the whole surface is thin so as to be no more than 50 μ m as mentioned above, an

extraction of a plasticizer for forming a pore may be easily and quickly completed. In case of the conventional Bellcore process, a polymer membrane is formed to a thickness of about 50-100 μm , in order to prevent a short circuit, so that a complete extraction of the plasticizer is difficult and a long period of time equal to about 1 day is required for the extraction thereof. Due to a long period of time required for extraction, continuous process is impossible, however, the present invention solves the problem and continuous process can be accomplished.

FIG. 1 is a sectional view of the separation membrane prepared by coating the polymer solution directly onto the separation membrane according to the first method of the present invention. When the polymer solution is directly coated onto the supporting body 5 of the separation membrane, the polymer 7 is impregnated into the inside of the separation membrane because of a low viscosity thereof. The impregnated polymer is transformed in the porous polymer separation membrane through a process for forming a porosity.

FIG. 2 is a sectional view of the polymer separation membrane prepared by compressing the polymer membrane onto the separation membrane, according to the second method of the present invention. If the polymer membrane that has been formed thin is compressed onto the supporting body 5 of the separation membrane, an empty space, where the polymer 7 has not been implanted, is formed, so that ionic conductivity and capability for impregnation with electrolytic solution are higher than a case of coating the polymer onto the supporting body of the separation membrane. Therefore, a more favorable method is to form a polymer separation membrane through compressing the pre-formed polymer membrane onto the separation membrane. However, the method for direct coating the polymer onto the separation membrane is also applicable in the present invention.

Thus prepared polymer separation membrane as mentioned above can be applied to a lithium polymer secondary battery, a capacitor, a sensor and the like.

The method for manufacturing the lithium polymer secondary battery by using the polymer separation membrane is as follows.

In order to attach the polymer separation membrane prepared according to the above-mentioned methods to an electrode, an adhesive polymer binder is coated
5 onto the polymer separation membrane. The polymer binder is partially coated by a spray method, a dipping method, a doctor blade method, a screen-printing method, an ink jet printing method and the like. Through the partial coating process, a good adhesiveness may be obtained and the electrolytic solution is easily implanted into an empty space formed between the polymer separation membrane and the electrode,
10 so that a cell having a high capacity and a good cycle-life characteristic can be manufactured.

The polymer binder is coated in such a manner that about 1-80% of the surface of the separation membrane on which the polymer membrane is formed is covered. If less than 1% of the surface of the porous polymer membrane is covered, a uniform
15 adhesiveness between the electrode and the separation membrane can hardly be obtained. If more than 80% of the surface of the porous polymer membrane is covered, an impregnation of an electrolyte into the inside of the electrode and the separation membrane becomes difficult. More preferably, the polymer binder is coated in such a manner that about 3-30% of the surface of the porous polymer
20 membrane is covered.

The following materials can be used for the polymer binder material without exemption.

For example, as the polymer binder material that can be used in the present invention, butadiene-based polymers including polyacrylonitrile-butadiene rubber
25 (NBR), polystyrene-butadiene rubber (SBR), polystyrene-butadiene-styrene rubber (SBS), acrylonitrile-butadiene-styrene rubber (ABS), polybutadiene, etc.; synthetic or natural rubbers including polydimethyl siloxane, polyisoprene, polychloroprene,

polyisobutylene, ethylenepropylene rubber, etc.; acryl-based resins including poly (alkyl acrylate), poly (alkyl methacrylate), poly (alkyl ethacrylate), copolymers thereof, and a combination thereof; polyether-based polymers including polyethylene oxide, polyoxymethylene, polypropylene oxide, copolymers thereof, and a combination thereof; fluoride-based polymers including polyvinylidene fluoride, polyvinylidene fluoride-hexafluoropropane, polychlorotrifluoroethylene and a copolymer thereof with ethylene, polytetrafluoroethylene, polyvinyl fluoride, and copolymers thereof; chloride-based polymers including poly (vinyl chloride) and poly (vinylidene chloride) and the like; polymers including a benzene ring such as polystyrene, phenol resin, etc.; polymers including OH group such as polyvinyl alcohol, polyhydroxy ethylmethacrylate, ethylene-vinyl alcohol copolymer, etc.; polymers including an acidic group such as polyacrylic acid, polystyrene sulfonic acid, polyamic acid, etc.; photocurable polymer such as polyvinyl cynamate, etc.; polymers including nitro group such as polyacrylonitrile, polymetacrylonitrile, copolymers or a mixture thereof, etc.; polyolefines such as polyethylene, polypropylene, etc.; polyvinyl acetal; polyvinyl ketal; polyvinyl butiral; polyvinyl formal; polyesters; polycarbonates; polyurethanes; polyamides; polyimides etc. can be used.

In addition to the above-described material, a copolymer thereof and a mixture thereof also can be used. More preferably, the rubber-based polymer, acryl-based resin, fluoride-based polymer and chloride-based polymer can be used.

FIG. 3 is a sectional view of the lithium polymer secondary battery prepared according to the above-mentioned method, wherein a thin polymer separation membrane that has a superior impregnation property with and a good maintenance property is provided on the surface of the supporting body of the separation membrane 5 and a polymer binder 6 is partially coated on the supporting body, so as to enhance an adhesiveness with the electrode. Since the polymer having a good

adhesive property is used, high temperature compression for the attachment of the electrode is not needed. Thus, the physical properties of the polymer are stabilized. According to the FIG. 3, as for the cathode, the electrode, wherein a cathode active material including metallic lithium, lithium alloy, synthetic graphite, natural graphite, petroleum coke, doped coke and the like has been coated on copper current collector 1 is used. As for the anode, the electrode, wherein anode active material including organic sulfur compound such as lithium-based LiCoO_2 , LiNiO_2 , LiCoNiO_2 , LiMn_2O_4 and sulfur has been coated on aluminum current collector is used. As for the current collector for supporting electrode active material, grid form of mesh or foil form can be used. The reason why a current collector in the foil form can be used is that since due to an excellent impregnation of the electrolytic solution into the empty space between the separation membrane and the electrode, the electrolytic solution can be very easily impregnated into cell so that any inferiority in impregnation characteristics of the electrolytic solution through the current collector is not so significant. Such superior impregnation characteristic of electrolytic solution improves productivity and thus the cell having uniform characteristics may be easily manufactured on the mass scale.

As the electrolytic solution used for manufacturing lithium polymer secondary battery, ethylenecarbonate (EC), propylene carbonate (PC), diethyl carbonate (DEC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), gamma-butyrolactone (γ -BL), and a mixture thereof can be used.

The lithium salt such as lithium perchlorate (LiClO_4), trifluoromethane sulfonate (LiCF_3SO_3), lithium borofluoride (LiBF_4), lithium hexafluorophosphate (LiPF_6), lithium arsenic hexafluoride (LiAsF_6), and a mixture thereof can be used in a concentration of about 1.0M to 2.0M. At this time, if the concentration of lithium salt is less than 1.0 M, the lithium content impregnated in the polymer electrolyte is insufficient, so that ion conductivity of electrolyte becomes lowered. Also, if the

concentration of lithium salt is more than 2M, the viscosity of the electrolyte is high, so that the over-voltage due to the concentration difference in the electrolyte becomes high. Also, problems in performance of lithium polymer at a low temperature are shown.

5 When manufacturing the cell, a packing cell and a winding cell may be manufactured. The porous separation membrane can be applied to general battery, secondary battery and capacitor, and the like. More preferably, the porous separation membrane can be applied to the cell that uses LiCoO_2 and LiMn_2O_4 as an anode in lithium secondary battery. Also, it can be applied to cell that uses an anode having a
10 sulfur or organic sulfur compound.

Finally, the present invention is developed such that it can be easily applied to mass production by separation of two capabilities of a polymer separation membrane. First, polyvinylidene fluoride-based porous polymer that is coated on a surface of the supporting body of the separation membrane increases affinity with
15 electrolytic solution, thereby enhancing impregnation with electrolytic solution and maintenance of an electrolytic solution on the interface. Also, the leakage of electrolytic solution that is characteristics of a general lithium polymer secondary battery is prevented and the stability problem due to short circuit is solved. Secondly, due to the use of a polymer binder having a good adhesiveness, a good adhesion
20 between electrode and separation membrane may be achieved, not at high temperature but at about room temperature $\sim 80^\circ\text{C}$, so that physical properties of the polymer are not changed and a cell having a reliability can be manufactured. Also, a cell can be manufactured, which has good characteristics of impregnation with an electrolytic solution through an empty space between separation membrane and
25 electrode formed due to partial coating and has a good maintenance characteristic of an electrolytic solution.

Since the adhesion can be implemented many times under a temperature that

the physical properties of polymer are unchanged by the adhesive polymer binder, during manufacture of a packing cell, a mono-cell type structure can be manufactured, not a bi-cell type structure which is a weak point of the conventional Bellcore method. Namely, conventionally, a cell was manufactured by packing a plural of unit electrodes having cathode/separation membrane/anode/separation membrane/cathode structure, to produce a bi-cell. However, in such a case, cathode and cathode makes contact with each other so that the optimal performance of the cell is difficult. However, in the present invention, a repeated compression with heat at a room temperature to 100°C may be performed, and thus a mono-cell having cathode/separation membrane/anode/separation membrane/cathode structure can be manufactured.

FIG. 4 is a schematic cross-sectional view of a packing type lithium secondary battery in the form of packing mono-cell including a separation membrane according to the present invention. According to FIG. 4, the cathode comprising a copper current collector 1 and a cathode active material 2 and the anode comprising aluminum current collector 3 and anode active material 4 are attached together in turn by a polymer binder 6 having a good adhesiveness. The polymer separation membrane wherein a thin porous polymer membrane is formed on the supporting body of the separation membrane is attached between the cathode and the anode.

The preferred examples of the present invention will be described in more detail, below. However, it should be understood that the present invention is not limited to the following examples.

<Example 1>

As PVdF copolymer (Kynar 2801: trade name manufactured by Elf Atochem Co. Ltd.), dibutylphthalate (DBP) and silica in a ratio of 2:3:1 by weight were added into acetone solvent of 80 wt.% and the resultant was stirred for 3 hours at 60

°C. The mixed polymer solution was transformed into a layer on a Mylar film (trade name available as a polyester film) on which silicon had been coated by a doctor blade method. At this time, the thickness of thus obtained layer was 6-10 μm . The polymer layer was compressed on an woven separation membrane (TF4035: trade name manufactured by Nippon Kodashi Corp.) as the supporting body at a temperature of 100°C and at a velocity of 10m/min. At this time, a roller having elastic rubber attached therewith was used. A thickness of the completed separation membrane polymer was prepared so as to have a thickness of 1-2 μm . This improved the problem of a thick thickness resulted from a manufacturing method for a conventional polymer battery.

The manufactured polymer separation membrane was immersed into methanol for about 1 min., so as to eliminate a plasticizer. Polybutylmethacrylate dissolved in acetone at 10 wt.% was dispersed into the prepared separation membrane through a spray method. The separation membrane on which polybutylmethacrylate had been coated was passed through a drying furnace, so as to eliminate acetone. Then, the packing cell was completed through a thermal compression of the separation membrane on the anode and the cathode with heat at temperature of 80°C. The compressed electrodes with heat were left under vacuum for about one day at temperature of 100-120°C, so as to remove water content and impurities. Under a temperature less than 120°C, the physical properties of the polymer layer within the separation membrane were not changed. As for anode, LiCoO_2 and as for cathode, MCMB were used as active materials. Then, 1M of LiPF_6 in EC/PC/DMC = 2/1/2 electrolytic solution was added into the cell and thus obtained cell was put into an aluminum laminated pack. Then, a sealing process was implemented.

<Example 2>

Without using silica as an inorganic additive, copolymer (Kynar 2801: trade name manufactured by Elf Atochem) and dibuthylphthalate (DBP) as polyvinylidene fluoride based polymer of 2/3 by weight were added into acetone solvent of 80 wt. %. The resultant was stirred for 3 hours at temperature of 60°C.

5 The mixed polymer solution was transformed into a layer on Mylar film (a kind of a polyester film) on which silicon had been coated by using a doctor blade method. At this time, the thickness of thus formed polymer layer was 6-10 μm . The polymer layer was compressed onto a woven separation membrane (TF4035: trade name manufactured by Nippon Kodashi Corp.) as the supporting body at a temperature of

10 140°C and at velocity of 6m/min. At this time, a roller having elastic rubber attached therewith was used. A thickness of the completed separation membrane was prepared so thin as to have a thickness of 1-2 μm .

The manufactured polymer separation membrane was immersed in methanol for about 1min., so as to eliminate a plasticizer. Polybutadiene-styrene rubber was

15 dispersed into water into which a surfactant had been added. The concentration of the polymer component was 8% by weight. The rubber solution was sprayed on the surface of the polymer separation membrane by using a spray gun. The rubbed coated membrane was passed through a drying furnace, so as to eliminate a solvent. The resultant was subsequently compressed at a room temperature, to thereby

20 complete the electrode. After the residual water contents thereof was eliminated, 1M of LiPF_6 in EC/PC/DMC = 2/1/2 electrolytic solution was added into the cell and thus obtained cell was put into an aluminum laminated pack. Then, a sealing process was implemented.

25 <Example 3>

Kynar 741 (trade name manufactured by Elf Atochem Inc.) as polyvinylidene fluoride based polymer and silica of 2/3 by weight ratio were mixed for 24 hours in

dried state through ball mixing. Then, the resultant was added into acetone solution of 80 wt. % and was subsequently stirred. At this time, plasticizer was not added thereto. The mixed polymer was coated directly onto a woven separation membrane (TF4035: trade name manufactured by Nippon Kodashi Corp.) as a supporting body.

- 5 In order to form pores in the polymer separation membrane that had passed through drying furnace so as to remove solvent, the membrane was immersed into methanol that is a nonsolvent for about 1 min. so as to form pores. Thus, in the same manner as in Example 1, the manufactured separation membrane was assembled to thereby complete a cell.

10

<Example 4>

- The same procedure as in Example 1 was implemented except that a non-woven polyolefin membrane was used as supporting body for the separation membrane. At this time, the non-woven polyolefin membrane may be applied to the present invention, but it is inferior in capabilities for impregnation with the electrolytic solution and maintaining characteristics for the electrolytic solution as compared with a woven separation membrane.

<Example 5>

- 20 The same procedure as in Example 1 was implemented except that woven PTFE (Gore-Tex PTFE separator: trade name manufactured by W. L. Gore & Associate) membrane was used as a supporting body for separation membrane. At this time, it could be noted that the characteristic in strength, which is one of weak point of PTFE was improved by coating the polymer layer.

- 25 The performance test with respect to the obtained cell was implemented as below.

FIG. 5 illustrates a relationship between a thickness-reducing rate of polymer

membrane when manufacturing a cell according to Example 1 and a final polymer membrane after extracting a plasticizer, and a polymer content according to the thickness changes.

FIG. 6 illustrates a cycle-life characteristic during charging and discharging according to the time required for extracting the plasticizer, when the polymer separation membrane was manufactured according to Example 1. According to FIG. 6, when an extracting process was performed for about 1 min., almost the plasticizer could be removed. It can be noted that the extraction was almost sufficiently completed in 5 min. When a thickness of the separation membrane was less than 10 μm , extraction of a plasticizer and formation of pores by a nonsolvent was advantageously performed. Since the extraction process of plasticizer was implemented before the compression to electrode, the residual plasticizer could be completely removed. Namely, according to the present invention, since the thickness of the polymer was thin and the solvent treatment process was implemented before electrode and separation membrane were compressed together, the time period required for immersing in solvent for extraction could be reduced. Therefore, the drastic increase in the mass production rate was obtained, which had been regarded as a weak point, and the manufacturing process can be implemented continuously. Also, since the separation membrane was used for the supporting body, the shrinkage of the polymer can be prevented.

FIG. 7 is a voltage profile dependent on time during charging and discharging the lithium polymer battery by 0.2 C rates according to Example 1 of the present invention. FIG. 7 shows general lithium secondary voltage characteristics wherein charging is comprised of a constant current area and a 4.2V constant voltage area. When the area of the constant voltage is smaller, lower resistance and better performance are shown. FIG. 7 shows that the cell has excellent performance through showing the low constant voltage area.

FIG. 8 shows charging and discharging efficiencies dependent on cycle during charging and discharging the lithium polymer battery by 1.0 C rate according to Example 1 of the present invention. Since an average charging-discharging efficiency is 99.9% in the figure, excellent cycle-life characteristic could be noted.

5 FIG. 9 shows a discharging capacity dependent on cycle during charging and discharging the lithium polymer battery by 1.0 C rate according to Example 1 of the present invention. The cycle-life characteristic more than 90% after 300 cycles could be noted as compared with the initial capacity.

FIG.10 illustrates a discharging capacity when lithium polymer battery prepared
10 by Example 4 was charged and discharged at a rate of 1C. When compared with FIG. 9, the cycle-life characteristic is somewhat lowered. However, this also may be regarded as being excellent.

FIG. 11 is a discharging capacity dependent on cycle during charging and discharging the lithium polymer battery by 1.0 C rate according to Example 5 of the
15 present invention.

As described above, according to the present invention, the polymers having two kinds of performance are applied separately, so that the mass production is improved. Non-uniformity on the process can be minimized by forming a polymer layer having a thin thickness by using the first polymer composition applied to the
20 present invention, polyvinylidene fluoride-based polymer thin. Polyvinylidene fluoride-based polymer layer improves the impregnation with an electrolytic solution and the affinity with the electrolytic solution, so that the impregnation characteristics and maintenance characteristics with the electrolytic solution are enhanced. Also, since the extracting process is implemented not after but before the
25 compression to the electrode and a thickness of polymer layer is thin, a plasticizer can be completely eliminated. Also, since the short time period is required for the compression and extraction of a plasticizer, the manufacturing process can be

performed quickly.

Since the separation membrane is used as a supporting body, the shrinkage of the polymer membrane that occurs during the extraction of a plasticizer can be prevented and the separation membrane having a stable physical property can be manufactured. Additionally, since the short circuit can be prevented, the battery
5 suitable for the manufacturing process can be manufactured. Also, the plasticizer can be removed easily due to the thin polymer membrane, so that the polymer cell having stable performance may be manufactured.

The cell is manufactured by using the polymer separation membrane on which
10 an adhesive polymer binder is entirely or partially coated. Due to the use of the polymer binder having an excellent adhesiveness, the adhesion can be implemented even at a low temperature, not a high temperature resulting in changes in physical properties thereof. Additionally, since the adhesion between the electrode and the polymer separation membrane is achieved as a spot adhesion, an empty space
15 between the electrode and the polymer separation membrane is formed so that a cell having an excellent characteristic of impregnation with electrolytic solution and good performance may be manufactured.

While the present invention is described in detail referring to the attached embodiments, various modifications, alternate constructions and equivalents may be
20 employed without departing from the true scope of the present invention.

Claims

1. An electrochemical cell comprising:
an anode;
5 a cathode; and
a separation membrane which is installed between the anode and the cathode,
said separation membrane including a supporting body of said separation membrane,
a polymer membrane formed on the supporting body, and a polymer binder
membrane formed on the polymer membrane, said supporting body including a
10 polyvinylidene fluoride-based polymer.
2. An electrochemical cell as claimed in claim 1, wherein a thickness of
the polymer membrane is about 1 to 50 μm .
- 15 3. An electrochemical cell as claimed in claim 1, wherein the
polyvinylidene fluoride-based polymer includes a polyvinylidene fluoride
copolymer including a hexafluoropropane (HFP) unit of about 8-25 % range.
4. An electrochemical cell as claimed in claim 1, wherein the polymer
20 binder membrane is coated on a surface of the polymer membrane such that the
polymer binder membrane covers about 1-80 % of the surface of the polymer
membrane.
5. An electrochemical cell as claimed in claim 1, wherein the polymer
25 membrane further comprises an inorganic filler by about 0.5-2 times of a weight of
the polyvinylidene fluoride-based polymer, and the inorganic filler is at least any
one selected from the group consisting of SiO_2 , zeolite, and Al_2O_3 .

6. An electrochemical cell as claimed in claim 1, wherein the supporting body of the polymer separation membrane is any one selected from the group consisting of non-woven polyethylene, non-woven polypropylene, fibrous PTFE, polyester non-woven fabric, solvent-spun-rayon, regenerated cellulose fiber, glass fiber, manila hemp, sisal pulp and kraft pulp.

7. An electrochemical cell as claimed in claim 1, wherein the polymer binder is at least any one selected from the group consisting of:

10 i) butadiene-based polymers including polyacrylonitrile-butadiene rubber (NBR), polystyrene-butadiene rubber (SBR), polystyrene-butadiene-styrene rubber (SBS), acrylonitrile-butadiene-styrene rubber (ABS), polybutadiene;

ii) synthetic or natural rubbers including polydimethyl siloxane, polyisoprene, polychloroprene, polyisobutylene, and ethylenepropylene rubber;

15 iii) acryl-based resins including poly (alkyl acrylate), poly (alkyl methacrylate), poly (alkyl ethacrylate), copolymers thereof, and a combination thereof;

iv) fluoride-based polymers including polyvinylidene fluoride, polyvinylidene fluoride-hexafluoropropane, polychloro trifluoroethylene and a copolymer thereof with ethylene, polytetrafluoro ethylene, polyvinyl fluoride, and copolymers thereof;

20 and

v) chloride-based polymers including poly (vinyl chloride) and poly (vinylidene chloride).

8. An electrochemical cell as claimed in claim 1, wherein the electrochemical cell is mono cell type wherein the anode, the polymer separation membrane, and the cathode are successively packed.

9. An electrochemical cell as claimed in claim 1, wherein an anode current collector for supporting the anode and a cathode current collector for supporting the cathode are in a mesh or foil type.

5 10. A method for manufacturing an electrochemical cell comprising the steps of:

forming a polymer membrane including a polyvinylidene fluoride-based polymer onto a supporting body of a polymer separation membrane;

10 forming a polymer binder membrane by coating a polymer binder on the polymer membrane; and

thermally compressing an anode and a cathode on the polymer binder membrane at a temperature in a range of about a room temperature to 80 °C.

15 11. A method for manufacturing an electrochemical cell as claimed in claim 10, wherein the polymer membrane is manufactured by

preparing a polymer solution by mixing the polyvinylidene fluoride-based polymer of 100 parts by weight, a solvent of about 100-3,000 parts by weight, and a plasticizer of about 100-1,000 parts by weight;

20 coating the polymer solution onto the supporting body of the separation membrane;

volatilizing the solvent from the coated polymer solution; and
extracting the plasticizer using an extraction solvent.

25 12. A method for manufacturing an electrochemical cell as claimed in claim 10, wherein the plasticizer is dibutylphthalate or dimethyladipate.

13. A method for manufacturing an electrochemical cell as claimed in

claim 10, wherein the polymer membrane is manufactured by

preparing the polymer solution by mixing the polyvinylidene fluoride-based polymer of 100 parts by weight with a solvent of about 100-3,000 parts by weight ;

coating the prepared polymer solution onto the supporter of the separation
5 membrane;

volatilizing the solvent from the dispersed polymer solution; and
forming a pore by using a nonsolvent.

14. A method for manufacturing an electrochemical cell as claimed in
10 claim 10, wherein the polymer membrane is manufactured by

preparing the polymer solution by mixing the polyvinylidene fluoride-based polymer of 100 parts by weight, the solvent of about 100-3,000 parts by weight, and the plasticizer of about 100-1,000 parts by weight;

coating the prepared polymer solution on the separate membrane to form a
15 layer by using a doctor blade method;

attaching the coated membrane to the supporting by a thermal compression at a temperature in a range of about room temperature to 130 °C; and

extracting the plasticizer using an extracting solvent.

20 15. A method for manufacturing an electrochemical cell as claimed in claim 14, wherein a compression ratio is about 1-75 % based on a whole thickness.

16. A method for manufacturing an electrochemical cell as claimed in claim 14, wherein the supporting of the separation membrane is a polyester film on
25 which silicon is coated.

17. A method for manufacturing an electrochemical cell as claimed in

claim 14, wherein the plasticizer is dibutylphthalate or dimethyladipate.

18. A method for manufacturing an electrochemical cell as claimed in claim 10, wherein the polymer membrane is manufactured by

5 preparing the polymer solution by mixing the polyvinylidene fluoride polymer of 100 parts by weight with a solvent of about 100-3,000 parts by weight;

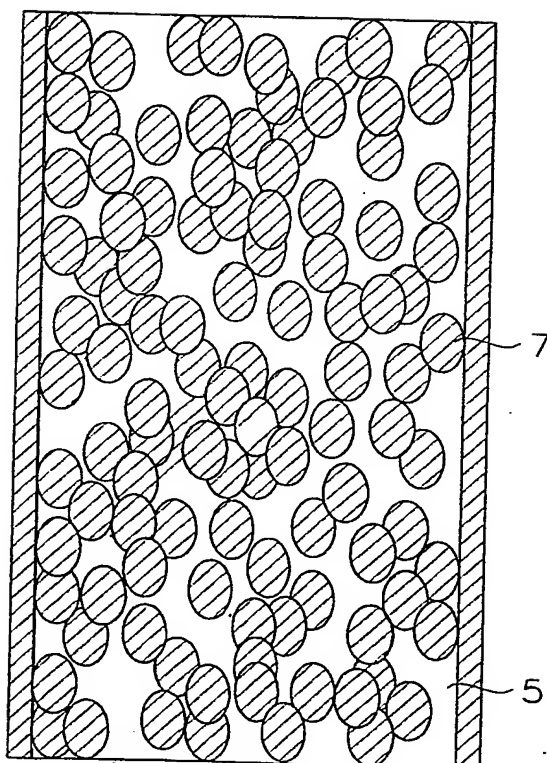
coating the prepared polymer solution on the separate membrane to form a layer by using a doctor blade method;

10 attaching the coated membrane to the supporting body of the separation membrane by a thermal compression at a temperature in the range of about room temperature to 130 °C; and

forming a pore by using a nonsolvent.

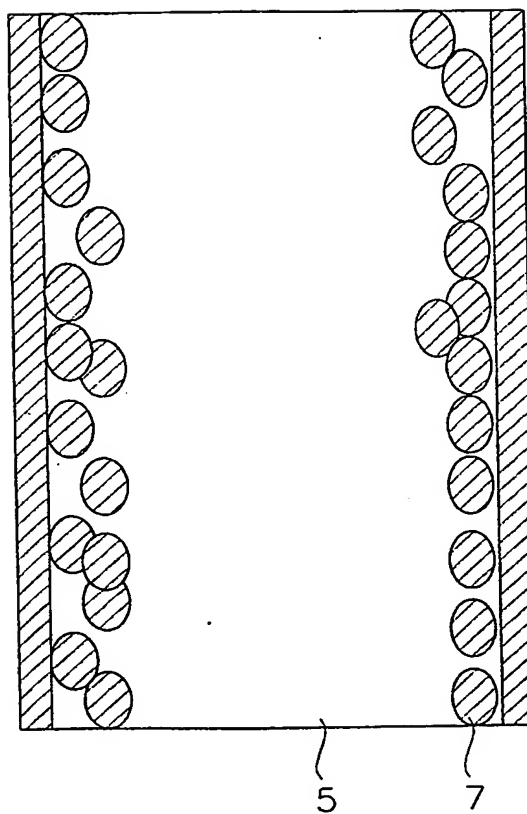
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FIG. 1



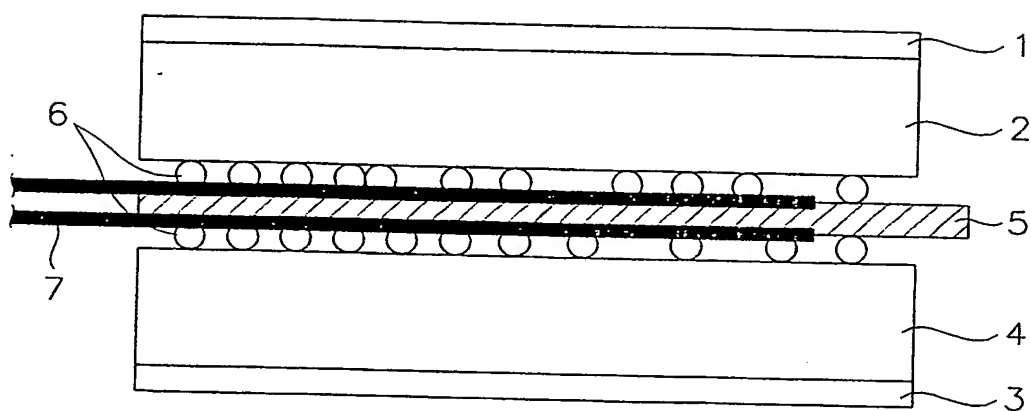
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FIG. 2



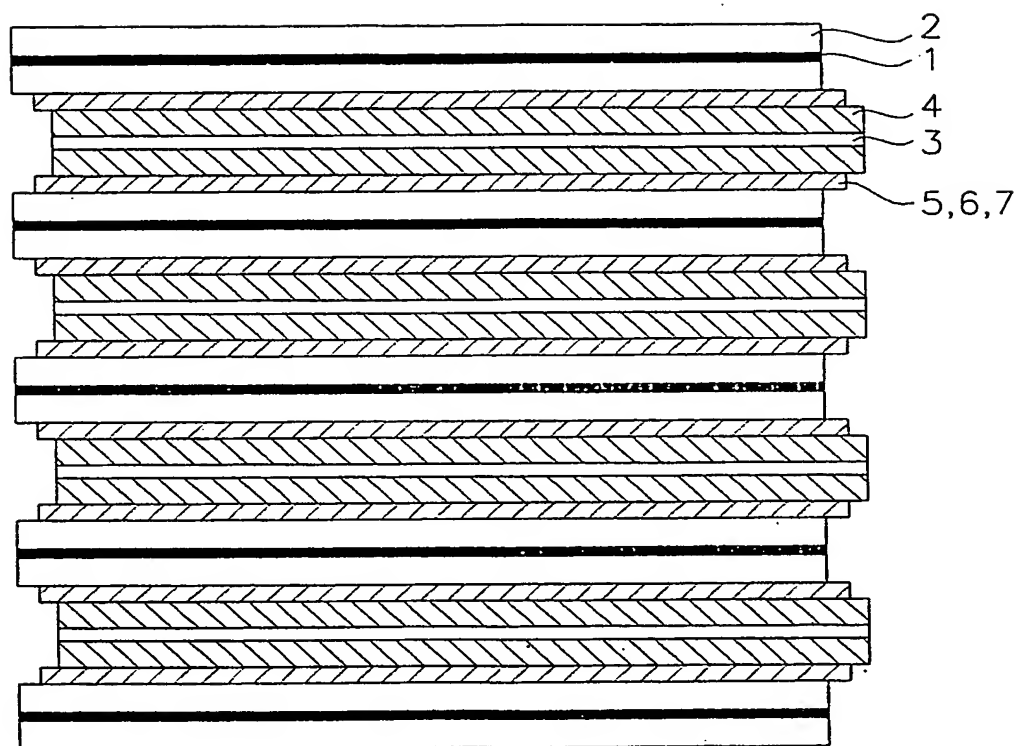
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FIG. 3



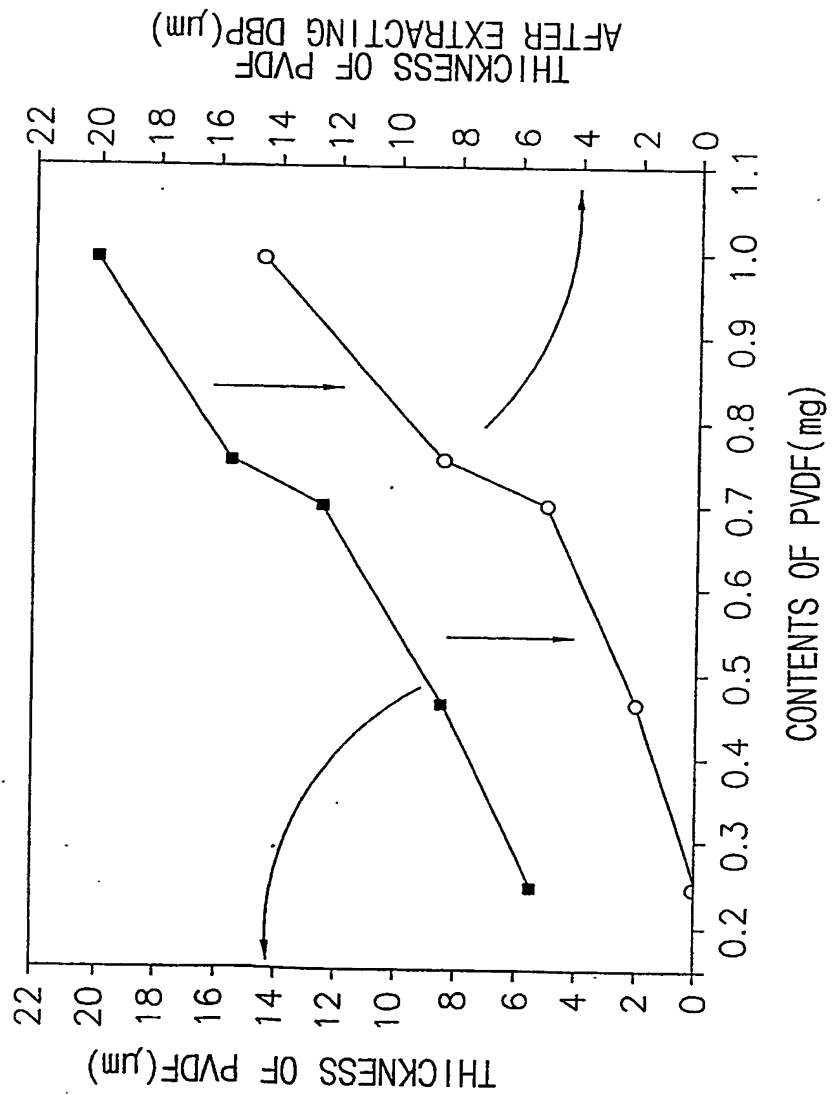
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FIG. 4



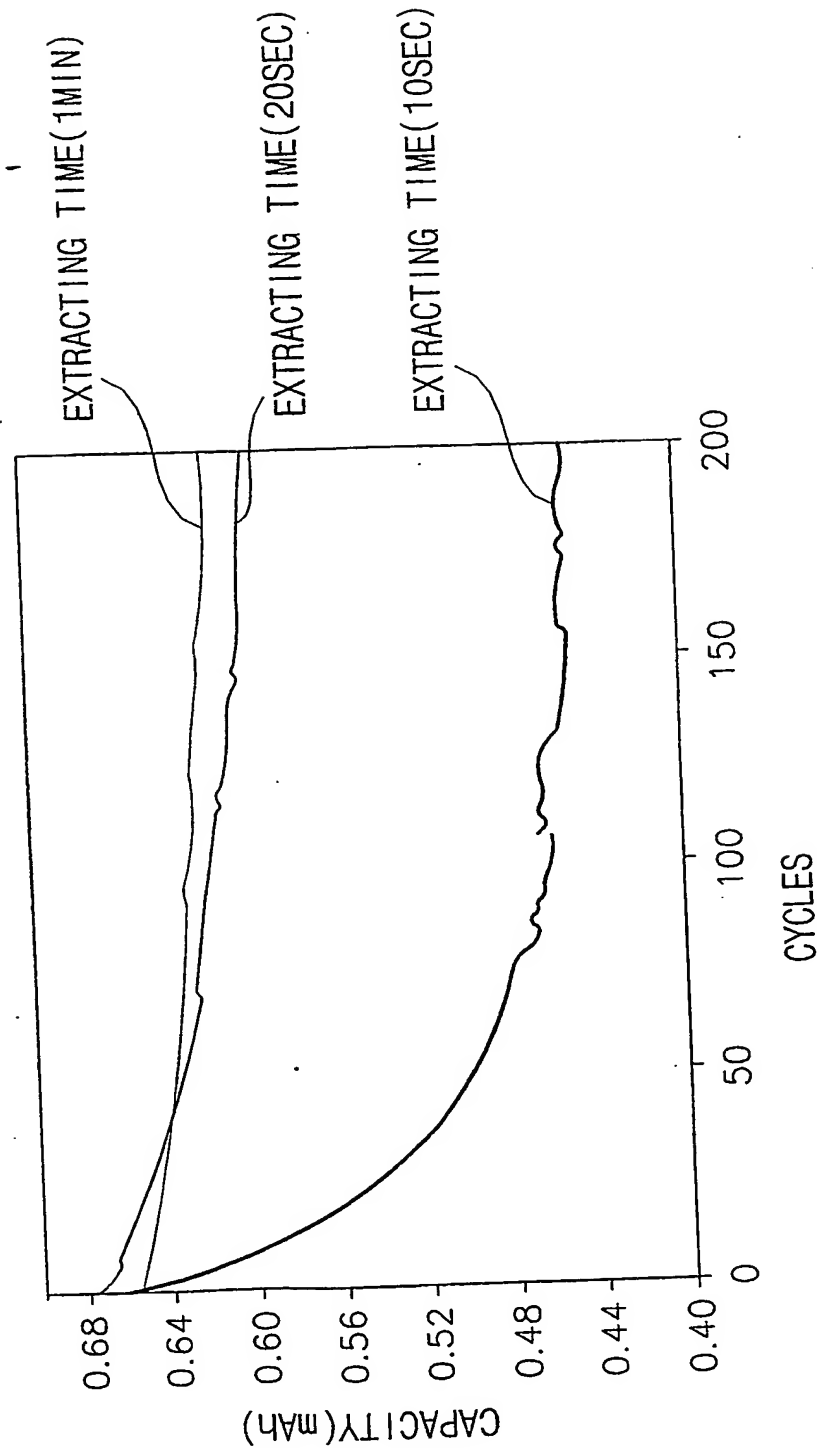
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FIG. 5



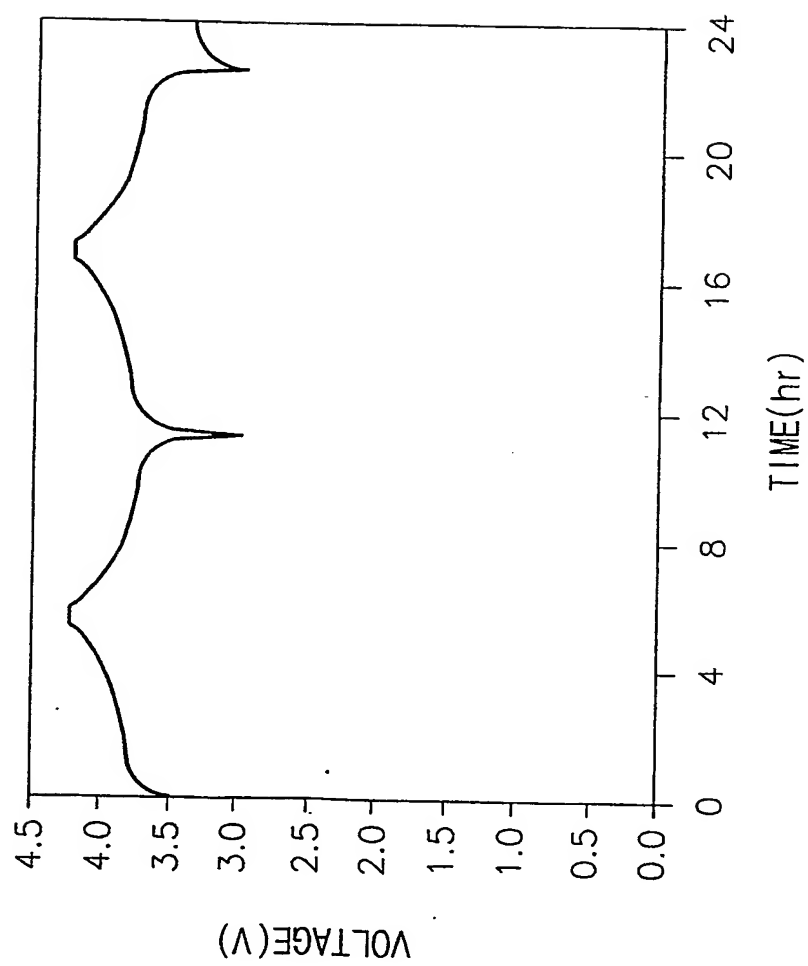
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FIG. 6



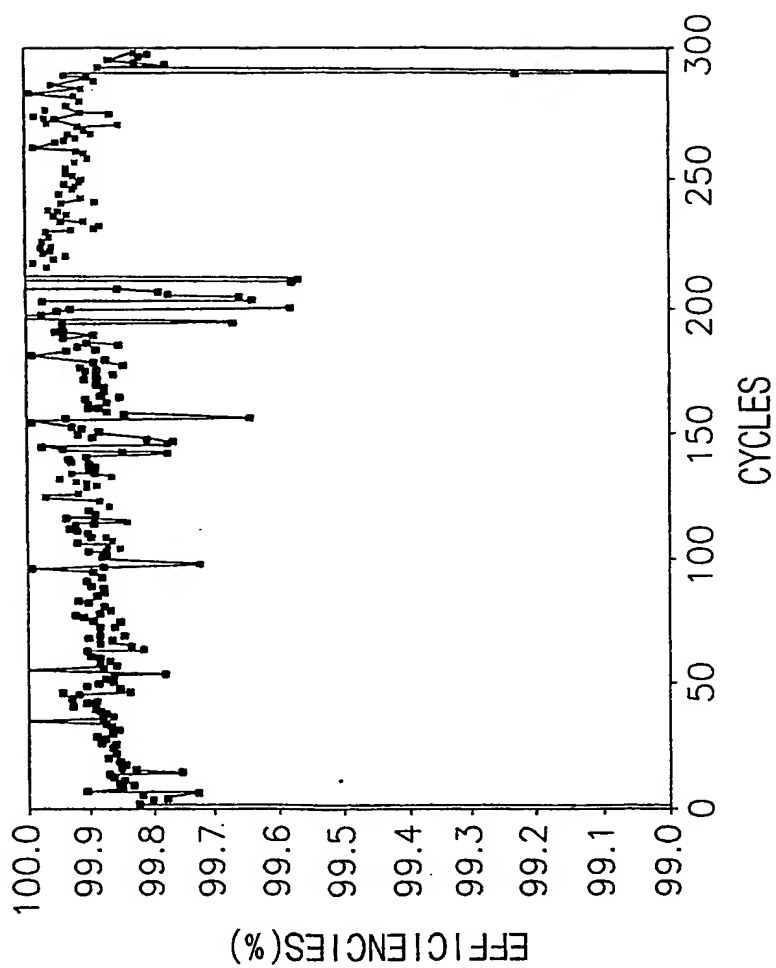
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FIG. 7



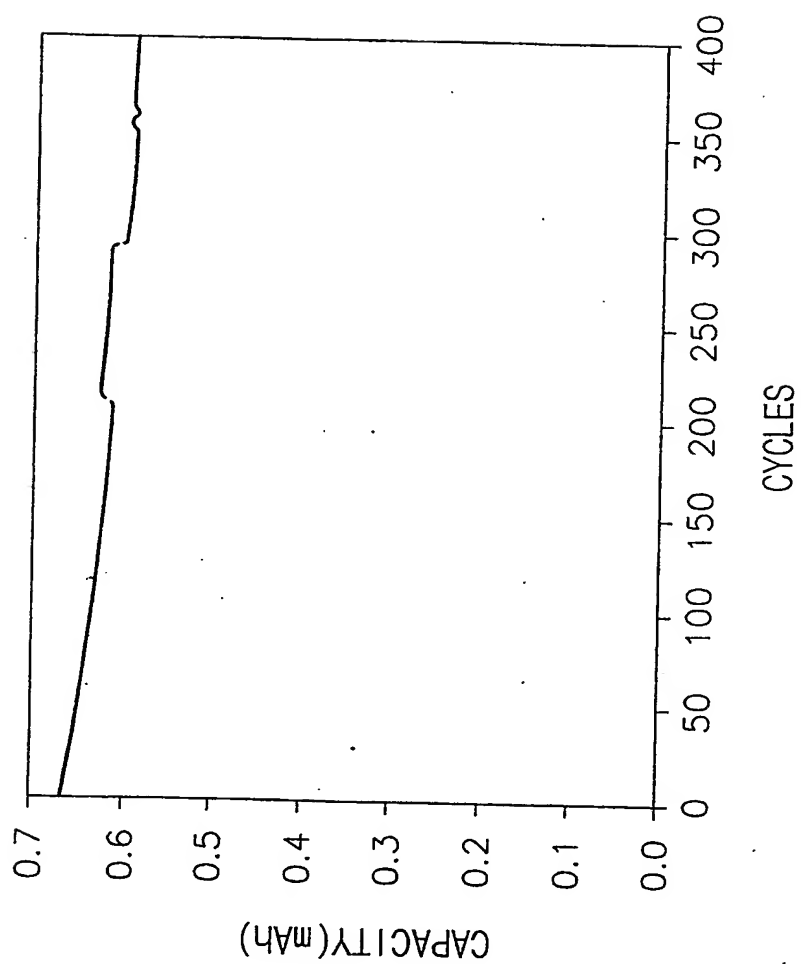
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FIG. 8



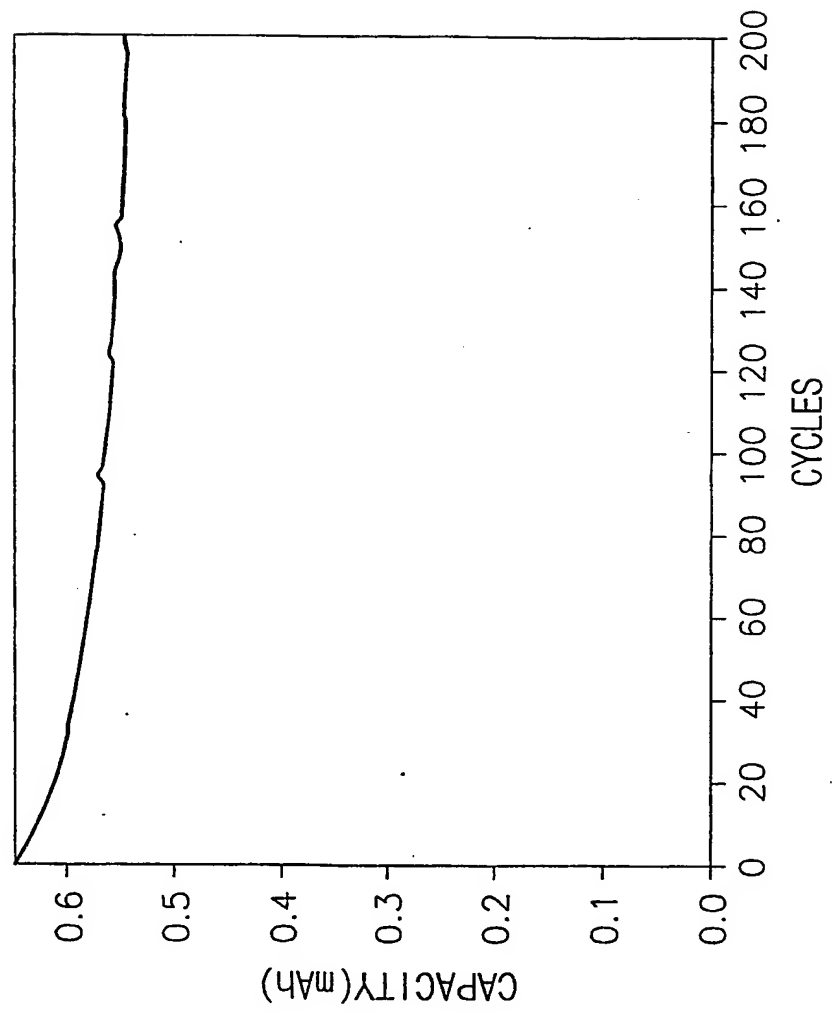
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FIG. 9



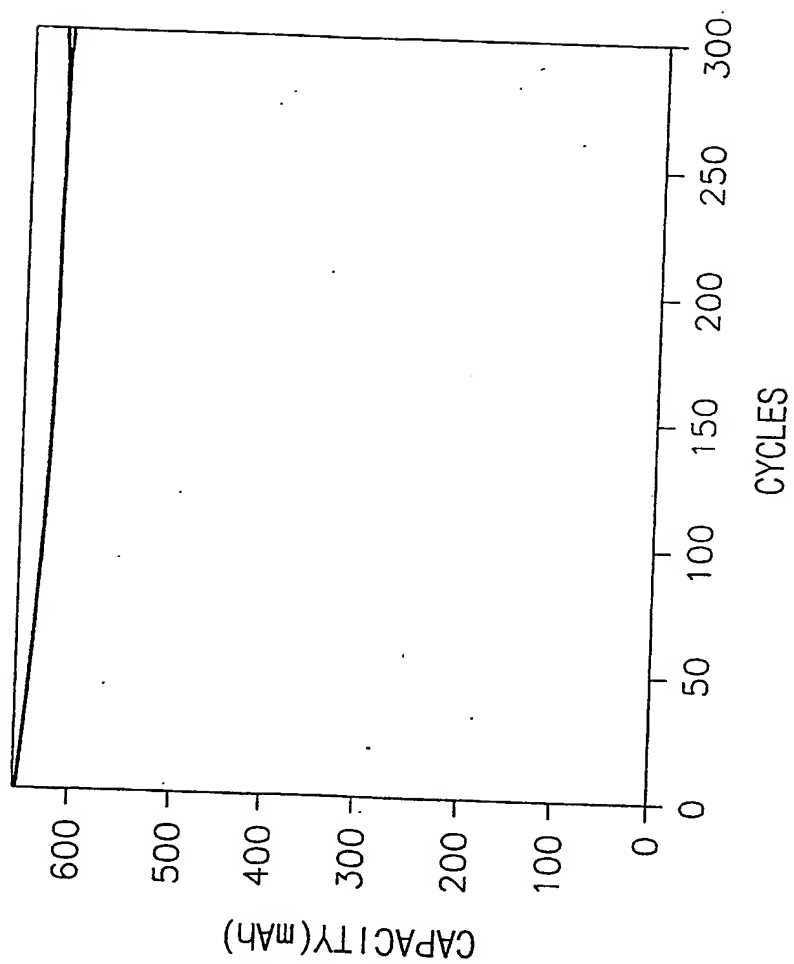
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FIG. 10



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FIG. 11



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR02/00310

A. CLASSIFICATION OF SUBJECT MATTER

IPC7 H01M 2/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01M 2/16

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean patents and applications for inventions since 1975

Korean Utility models and applications for Utility since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

KIPASS, MIMOSA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KR 2002-0019608 A(GS MELCO TECH Co.LTD 12, MAR, 2002) See the entire sentence	1,10
A	KR 2001-0055968 A(Co. LTD LG. C.I. 04, JULY, 2001) See the entire sentence	1,10
E A	KR 2002-0078660 A(SAM SUNG SDI Co.LTD 19, OCT, 2002) See the entire sentence	1,10
EA	KR 2002-0071203 A(Co. LTD LG CHEMISTRY 12, SEP, 2002) See the entire sentence	1,10

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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29 OCTOBER 2002 (29.10.2002)

Date of mailing of the international search report

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Name and mailing address of the ISA/KR



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